

NO-A090 013

OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY F/G 7/3  
SYNTHESIS OF TETRAPHENYLSTRANNACY-CLOPENTADIENES (STANNOLES). I--ETC(U)  
OCT 80 W - RHEE, J J ZUCKERMAN N00014-77-C-0432  
TR-22 NL

UNCLASSIFIED

1 of 1  
AC  
09/20/82



END  
DATE  
FILMED  
10 80  
DTIC

AD A090013

LEVEL

12

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-639

TECHNICAL REPORT NO. 22

Synthesis of Tetraphenylstrannacyclopentadienes (Stannoies).

III. Attempted Route to the Parent Stannoies  
Through Closure of 1,4-Dichlorobuta-1,3-diene

by

W. -Z. Min/Rhee and J. J. Zuckerman

Prepared for Publication

in

The Journal of Organometallic Chemistry

University of Oklahoma  
Department of Chemistry  
Norman, Oklahoma 73019

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited

DDC FILE COPY

80 10 6 032

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 22	2. GOVT ACCESSION NO. AD-A090 013	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis of Tetraphenylstannacyclopentadienes (Stannoies). III. Attempted Route to the Parent Stannoies Through Closure of 1,4-Dichlorobuta-1,3-diene		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) W.-Z. Min Rhee and J. J. Zuckerman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oklahoma Department of Chemistry Norman, Oklahoma 73019		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0432
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-636
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 1 October, 1980
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for Public Release, Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  Prepared for publication in the Journal of Organometallic Chemistry		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Organotin derivatives, Tetraorganotins, Infrared, Nuclear magnetic resonance, Mössbauer spectroscopy, Mass spectroscopy, Tin-119m Mössbauer spectroscopy, Metalloles, Stannoies, Siloles, 1,4-Dichlorobuta-1,3-diene, Lithiation, Organochlorosilanes, Organotin chlorides, Dehydrochlorination, Multiple bond migration, 1,4-Bis(trimethylsilyl)buta-1,3-diyne, 1,4-Bis(trimethyltin)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 1,4-Dichlorobuta-1,3-diene has been lithiated and reacted with organosilyl and tin chlorides. Only polymerized starting material, rather than the hoped for parent sila- and stannacyclopentadienyl (silole and stannole) ring systems result from the action of the lithiated material on diorganodichlorosilanes and diorganotin dichlorides. Addition of the lithiated butadiene to trimethylchlorosilane and trimethyltin chloride yields products resulting from dehydrochlorination and multiple bond migration in the starting dichlorobutadiene.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. butatriene, Poly-1,4-dichlorobutadiene.

Accession For  
1915-1918  
1919-1920  
1921-1922  
1923-1924  
1925-1926  
1927-1928  
1929-1930  
1931-1932  
1933-1934  
1935-1936  
1937-1938  
1939-1940  
1941-1942  
1943-1944  
1945-1946  
1947-1948  
1949-1950  
1951-1952  
1953-1954  
1955-1956  
1957-1958  
1959-1960  
1961-1962  
1963-1964  
1965-1966  
1967-1968  
1969-1970  
1971-1972  
1973-1974  
1975-1976  
1977-1978  
1979-1980  
1981-1982  
1983-1984  
1985-1986  
1987-1988  
1989-1990  
1991-1992  
1993-1994  
1995-1996  
1997-1998  
1999-2000  
2001-2002  
2003-2004  
2005-2006  
2007-2008  
2009-2010  
2011-2012  
2013-2014  
2015-2016  
2017-2018  
2019-2020  
2021-2022  
2023-2024  
2025-2026  
2027-2028  
2029-2030  
2031-2032  
2033-2034  
2035-2036  
2037-2038  
2039-2040  
2041-2042  
2043-2044  
2045-2046  
2047-2048  
2049-2050  
2051-2052  
2053-2054  
2055-2056  
2057-2058  
2059-2060  
2061-2062  
2063-2064  
2065-2066  
2067-2068  
2069-2070  
2071-2072  
2073-2074  
2075-2076  
2077-2078  
2079-2080  
2081-2082  
2083-2084  
2085-2086  
2087-2088  
2089-2090  
2091-2092  
2093-2094  
2095-2096  
2097-2098  
2099-2100  
2101-2102  
2103-2104  
2105-2106  
2107-2108  
2109-2110  
2111-2112  
2113-2114  
2115-2116  
2117-2118  
2119-2120  
2121-2122  
2123-2124  
2125-2126  
2127-2128  
2129-2130  
2131-2132  
2133-2134  
2135-2136  
2137-2138  
2139-2140  
2141-2142  
2143-2144  
2145-2146  
2147-2148  
2149-2150  
2151-2152  
2153-2154  
2155-2156  
2157-2158  
2159-2160  
2161-2162  
2163-2164  
2165-2166  
2167-2168  
2169-2170  
2171-2172  
2173-2174  
2175-2176  
2177-2178  
2179-2180  
2181-2182  
2183-2184  
2185-2186  
2187-2188  
2189-2190  
2191-2192  
2193-2194  
2195-2196  
2197-2198  
2199-2200  
2201-2202  
2203-2204  
2205-2206  
2207-2208  
2209-2210  
2211-2212  
2213-2214  
2215-2216  
2217-2218  
2219-2220  
2221-2222  
2223-2224  
2225-2226  
2227-2228  
2229-2230  
2231-2232  
2233-2234  
2235-2236  
2237-2238  
2239-2240  
2241-2242  
2243-2244  
2245-2246  
2247-2248  
2249-2250  
2251-2252  
2253-2254  
2255-2256  
2257-2258  
2259-2260  
2261-2262  
2263-2264  
2265-2266  
2267-2268  
2269-2270  
2271-2272  
2273-2274  
2275-2276  
2277-2278  
2279-2280  
2281-2282  
2283-2284  
2285-2286  
2287-2288  
2289-2290  
2291-2292  
2293-2294  
2295-2296  
2297-2298  
2299-2300  
2301-2302  
2303-2304  
2305-2306  
2307-2308  
2309-2310  
2311-2312  
2313-2314  
2315-2316  
2317-2318  
2319-2320  
2321-2322  
2323-2324  
2325-2326  
2327-2328  
2329-2330  
2331-2332  
2333-2334  
2335-2336  
2337-2338  
2339-2340  
2341-2342  
2343-2344  
2345-2346  
2347-2348  
2349-2350  
2351-2352  
2353-2354  
2355-2356  
2357-2358  
2359-2360  
2361-2362  
2363-2364  
2365-2366  
2367-2368  
2369-2370  
2371-2372  
2373-2374  
2375-2376  
2377-2378  
2379-2380  
2381-2382  
2383-2384  
2385-2386  
2387-2388  
2389-2390  
2391-2392  
2393-2394  
2395-2396  
2397-2398  
2399-2400  
2401-2402  
2403-2404  
2405-2406  
2407-2408  
2409-2410  
2411-2412  
2413-2414  
2415-2416  
2417-2418  
2419-2420  
2421-2422  
2423-2424  
2425-2426  
2427-2428  
2429-2430  
2431-2432  
2433-2434  
2435-2436  
2437-2438  
2439-2440  
2441-2442  
2443-2444  
2445-2446  
2447-2448  
2449-2450  
2451-2452  
2453-2454  
2455-2456  
2457-2458  
2459-2460  
2461-2462  
2463-2464  
2465-2466  
2467-2468  
2469-2470  
2471-2472  
2473-2474  
2475-2476  
2477-2478  
2479-2480  
2481-2482  
2483-2484  
2485-2486  
2487-2488  
2489-2490  
2491-2492  
2493-2494  
2495-2496  
2497-2498  
2499-2500  
2501-2502  
2503-2504  
2505-2506  
2507-2508  
2509-2510  
2511-2512  
2513-2514  
2515-2516  
2517-2518  
2519-2520  
2521-2522  
2523-2524  
2525-2526  
2527-2528  
2529-2530  
2531-2532  
2533-2534  
2535-2536  
2537-2538  
2539-2540  
2541-2542  
2543-2544  
2545-2546  
2547-2548  
2549-2550  
2551-2552  
2553-2554  
2555-2556  
2557-2558  
2559-2560  
2561-2562  
2563-2564  
2565-2566  
2567-2568  
2569-2570  
2571-2572  
2573-2574  
2575-2576  
2577-2578  
2579-2580  
2581-2582  
2583-2584  
2585-2586  
2587-2588  
2589-2590  
2591-2592  
2593-2594  
2595-2596  
2597-2598  
2599-2600  
2601-2602  
2603-2604  
2605-2606  
2607-2608  
2609-2610  
2611-2612  
2613-2614  
2615-2616  
2617-2618  
2619-2620  
2621-2622  
2623-2624  
2625-2626  
2627-2628  
2629-2630  
2631-2632  
2633-2634  
2635-2636  
2637-2638  
2639-2640  
2641-2642  
2643-2644  
2645-2646  
2647-2648  
2649-2650  
2651-2652  
2653-2654  
2655-2656  
2657-2658  
2659-2660  
2661-2662  
2663-2664  
2665-2666  
2667-2668  
2669-2670  
2671-2672  
2673-2674  
2675-2676  
2677-2678  
2679-2680  
2681-2682  
2683-2684  
2685-2686  
2687-2688  
2689-2690  
2691-2692  
2693-2694  
2695-2696  
2697-2698  
2699-2700  
2701-2702  
2703-2704  
2705-2706  
2707-2708  
2709-2710  
2711-2712  
2713-2714  
2715-2716  
2717-2718  
2719-2720  
2721-2722  
2723-2724  
2725-2726  
2727-2728  
2729-2730  
2731-2732  
2733-2734  
2735-2736  
2737-2738  
2739-2740  
2741-2742  
2743-2744  
2745-2746  
2747-2748  
2749-2750  
2751-2752  
2753-2754  
2755-2756  
2757-2758  
2759-2760  
2761-2762  
2763-2764  
2765-2766  
2767-2768  
2769-2770  
2771-2772  
2773-2774  
2775-2776  
2777-2778  
2779-2780  
2781-2782  
2783-2784  
2785-2786  
2787-2788  
2789-2790  
2791-2792  
2793-2794  
2795-2796  
2797-2798  
2799-2800  
2801-2802  
2803-2804  
2805-2806  
2807-2808  
2809-2810  
2811-2812  
2813-2814  
2815-2816  
2817-2818  
2819-2820  
2821-2822  
2823-2824  
2825-2826  
2827-2828  
2829-2830  
2831-2832  
2833-2834  
2835-2836  
2837-2838  
2839-2840  
2841-2842  
2843-2844  
2845-2846  
2847-2848  
2849-2850  
2851-2852  
2853-2854  
2855-2856  
2857-2858  
2859-2860  
2861-2862  
2863-2864  
2865-2866  
2867-2868  
2869-2870  
2871-2872  
2873-2874  
2875-2876  
2877-2878  
2879-2880  
2881-2882  
2883-2884  
2885-2886  
2887-2888  
2889-2890  
2891-2892  
2893-2894  
2895-2896  
2897-2898  
2899-2900  
2901-2902  
2903-2904  
2905-2906  
2907-2908  
2909-2910  
2911-2912  
2913-2914  
2915-2916  
2917-2918  
2919-2920  
2921-2922  
2923-2924  
2925-2926  
2927-2928  
2929-2930  
2931-2932  
2933-2934  
2935-2936  
2937-2938  
2939-2940  
2941-2942  
2943-2944  
2945-2946  
2947-2948  
2949-2950  
2951-2952  
2953-2954  
2955-2956  
2957-2958  
2959-2960  
2961-2962  
2963-2964  
2965-2966  
2967-2968  
2969-2970  
2971-2972  
2973-2974  
2975-2976  
2977-2978  
2979-2980  
2981-2982  
2983-2984  
2985-2986  
2987-2988  
2989-2990  
2991-2992  
2993-2994  
2995-2996  
2997-2998  
2999-3000  
3001-3002  
3003-3004  
3005-3006  
3007-3008  
3009-3010  
3011-3012  
3013-3014  
3015-3016  
3017-3018  
3019-3020  
3021-3022  
3023-3024  
3025-3026  
3027-3028  
3029-3030  
3031-3032  
3033-3034  
3035-3036  
3037-3038  
3039-3040  
3041-3042  
3043-3044  
3045-3046  
3047-3048  
3049-3050  
3051-3052  
3053-3054  
3055-3056  
3057-3058  
3059-3060  
3061-3062  
3063-3064  
3065-3066  
3067-3068  
3069-3070  
3071-3072  
3073-3074  
3075-3076  
3077-3078  
3079-3080  
3081-3082  
3083-3084  
3085-3086  
3087-3088  
3089-3090  
3091-3092  
3093-3094  
3095-3096  
3097-3098  
3099-3100  
3101-3102  
3103-3104  
3105-3106  
3107-3108  
3109-3110  
3111-3112  
3113-3114  
3115-3116  
3117-3118  
3119-3120  
3121-3122  
3123-3124  
3125-3126  
3127-3128  
3129-3130  
3131-3132  
3133-3134  
3135-3136  
3137-3138  
3139-3140  
3141-3142  
3143-3144  
3145-3146  
3147-3148  
3149-3150  
3151-3152  
3153-3154  
3155-3156  
3157-3158  
3159-3160  
3161-3162  
3163-3164  
3165-3166  
3167-3168  
3169-3170  
3171-3172  
3173-3174  
3175-3176  
3177-3178  
3179-3180  
3181-3182  
3183-3184  
3185-3186  
3187-3188  
3189-3190  
3191-3192  
3193-3194  
3195-3196  
3197-3198  
3199-3200  
3201-3202  
3203-3204  
3205-3206  
3207-3208  
3209-3210  
3211-3212  
3213-3214  
3215-3216  
3217-3218  
3219-3220  
3221-3222  
3223-3224  
3225-3226  
3227-3228  
3229-3230  
3231-3232  
3233-3234  
3235-3236  
3237-3238  
3239-3240  
3241-3242  
3243-3244  
3245-3246  
3247-3248  
3249-3250  
3251-3252  
3253-3254  
3255-3256  
3257-3258  
3259-3260  
3261-3262  
3263-3264  
3265-3266  
3267-3268  
3269-3270  
3271-3272  
3273-3274  
3275-3276  
3277-3278  
3279-3280  
3281-3282  
3283-3284  
3285-3286  
3287-3288  
3289-3290  
3291-3292  
3293-3294  
3295-3296  
3297-3298  
3299-3300  
3301-3302  
3303-3304  
3305-3306  
3307-3308  
3309-3310  
3311-3312  
3313-3314  
3315-3316  
3317-3318  
3319-3320  
3321-3322  
3323-3324  
3325-3326  
3327-3328  
3329-3330  
3331-3332  
3333-3334  
3335-3336  
3337-3338  
3339-3340  
3341-3342  
3343-3344  
3345-3346  
3347-3348  
3349-3350  
3351-3352  
3353-3354  
3355-3356  
3357-3358  
3359-3360  
3361-3362  
3363-3364  
3365-3366  
3367-3368  
3369-3370  
3371-3372  
3373-3374  
3375-3376  
3377-3378  
3379-3380  
3381-3382  
3383-3384  
3385-3386  
3387-3388  
3389-3390  
3391-3392  
3393-3394  
3395-3396  
3397-3398  
3399-3400  
3401-3402  
3403-3404  
3405-3406  
3407-3408  
3409-3410  
3411-3412  
3413-3414  
3415-3416  
3417-3418  
3419-3420  
3421-3422  
3423-3424  
3425-3426  
3427-3428  
3429-3430  
3431-3432  
3433-3434  
3435-3436  
3437-3438  
3439-3440  
3441-3442  
3443-3444  
3445-3446  
3447-3448  
3449-3450  
3451-3452  
3453-3454  
3455-3456  
3457-3458  
3459-3460  
3461-3462  
3463-3464  
3465-3466  
3467-3468  
3469-3470  
3471-3472  
3473-3474  
3475-3476  
3477-3478  
3479-3480  
3481-3482  
3483-3484  
3485-3486  
3487-3488  
3489-3490  
3491-3492  
3493-3494  
3495-3496  
3497-3498  
3499-3500  
3501-3502  
3503-3504  
3505-3506  
3507-3508  
3509-3510  
3511-3512  
3513-3514  
3515-3516  
3517-3518  
3519-3520  
3521-3522  
3523-3524  
3525-3526  
3527-3528  
3529-3530  
3531-3532  
3533-3534  
3535-3536  
3537-3538  
3539-3540  
3541-3542  
3543-3544  
3545-3546  
3547-3548  
3549-3550  
3551-3552  
3553-3554  
3555-3556  
3557-3558  
3559-3560  
3561-3562  
3563-3564  
3565-3566  
3567-3568  
3569-3570  
3571-3572  
3573-3574  
3575-3576  
3577-3578  
3579-3580  
3581-3582  
3583-3584  
3585-3586  
3587-3588  
3589-3590  
3591-3592  
3593-3594  
3595-3596  
3597-3598  
3599-3600  
3601-3602  
3603-3604  
3605-3606  
3607-3608  
3609-3610  
3611-3612  
3613-3614  
3615-3616  
3617-3618  
3619-3620  
3621-3622  
3623-3624  
3625-3626  
3627-3628  
3629-3630  
3631-3632  
3633-3634  
3635-3636  
3637-3638  
3639-3640  
3641-3642  
3643-3644  
3645-3646  
3647-3648  
3649-3650  
3651-3652  
3653-3654  
3655-3656  
3657-3658  
3659-3660  
3661-3662  
3663-3664  
3665-3666  
3667-3668  
3669-3670  
3671-3672  
3673-3674  
3675-3676  
3677-3678  
3679-3680  
3681-3682  
3683-3684  
3685-3686  
3687-3688  
3689-3690  
3691-3692  
3693-3694  
3695-3696  
3697-3698  
3699-3700  
3701-3702  
3703-3704  
3705-3706  
3707-3708  
3709-3710  
3711-3712  
3713-3714  
3715-3716  
3717-3718  
3719-3720  
3721-3722  
3723-3724  
3725-3726  
3727-3728  
3729-3730  
3731-3732  
3733-3734  
3735-3736  
3737-3738  
3739-3740  
3741-3742  
3743-3744  
3745-3746  
3747-3748  
3749-3750  
3751-3752  
3753-3754  
3755-3756  
3757-3758  
3759-3760  
3761-3762  
3763-3764  
3765-3766  
3767-3768  
3769-3770  
3771-3772  
3773-3774  
3775-3776  
3777-3778  
3779-3780  
3781-3782  
3783-3784  
3785-3786  
3787-3788  
3789-3790  
3791-3792  
3793-3794  
3795-3796  
3797-3798  
3799-3800  
3801-3802  
3803-3804  
3805-3806  
3807-3808  
3809-3810  
3811-3812  
3813-3814  
3815-3816  
3817-3818  
3819-3820  
3821-3822  
3823-3824  
3825-3826  
3827-3828  
3829-3830  
3831-3832  
3833-3834  
3835-3836  
3837-3838  
3839-3840  
3841-3842  
3843-3844  
3845-3846  
3847-3848  
3849-3850  
3851-3852  
3853-3854  
3855-3856  
3857-3858  
3859-3860  
3861-3862  
3863-3864  
3865-3866  
3867-3868  
3869-3870  
3871-3872  
3873-3874  
3875-3876  
3877-3878  
3879-3880  
3881-3882  
3883-3884  
3885-3886  
3887-3888  
3889-3890  
3891-3892  
3893-3894  
3895-3896  
3897-3898  
3899-3900  
3901-3902  
3903-3904  
3905-3906  
3907-3908  
3909-3910  
3911-3912  
3913-3914  
3915-3916  
3917-3918  
3919-3920  
3921-3922  
3923-3924  
3925-3926  
3927-3928  
3929-3930  
3931-3932  
3933-3934  
3935-3936  
3937-3938  
3939-3940  
3941-3942  
3943-3944  
3945-3946  
3947-3948  
3949-3950  
3951-3952  
3953-3954  
3955-3956  
3957-3958  
3959-3960  
3961-3962  
3963-3964  
3965-3966  
3967-3968  
3969-3970  
3971-3972  
3973-3974  
3975-3976  
3977-3978  
3979-3980  
3981-3982  
3983-3984  
3985-3986  
3987-3988  
3989-3990  
3991-3992  
3993-3994  
3995-3996  
3997-3998  
3999-4000  
4001-4002  
4003-4004  
4005-4006  
4007-4008  
4009-4010  
4011-4012  
4013-4014  
4015-4016  
4017-4018  
4019-4020  
4021-4022  
4023-4024  
4025-4026  
4027-4028  
4029-4030  
4031-4032  
4033-4034  
4035-4036  
4037-4038  
4039-4040  
4041-4042  
4043-4044  
4045-4046  
4047-4048  
4049-4050  
4051-4052  
4053-4054  
4055-4056  
4057-4058  
4059-4060  
4061-4062  
4063-4064  
4065-4066  
4067-4068  
4069-4070  
4071-4072  
4073-4074  
4075-4076  
4077-4078  
4079-4080  
4081-4082  
4083-4084  
4085-4086  
4087-4088  
4089-4090  
4091-4092  
4093-4094  
4095-4096  
4097-4098  
4099-4100  
4101-4102  
4103-4104  
4105-4106  
4107-4108  
4109-4110  
4111-4112  
4113-4114  
4115-4116  
4117-4118  
4119-4120  
4121-4122  
4123-4124  
4125-4126  
4127-4128  
4129-4130  
4131-4132  
4133-4134  
4135-4136  
4137-4138  
4139-4140  
4141-4142  
4143-4144  
41

Synthesis of Tetraphenylstannacyclopentadienes (Stannoles).

III. Attempted Route to the Parent Stannoles  
Through Closure of 1,4-Dichlorobuta-1,3-diene<sup>1</sup>

W.-Z. Min Rhee and J. J. Zuckerman\*

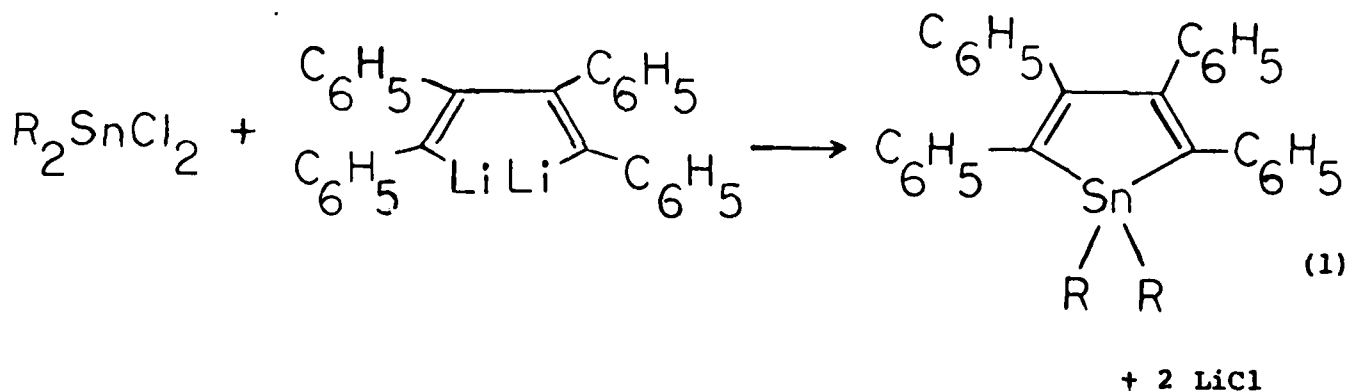
Department of Chemistry  
University of Oklahoma  
Norman, OK 73019

### Summary

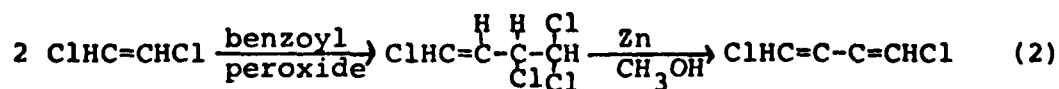
1,4-Dichlorobuta-1,3-diene has been lithiated and reacted with organosilyl and tin chlorides. Only polymerized starting material, rather than the hoped for parent sila- and stannacyclopentadienyl (silole and stannole) ring systems result from the action of the lithiated material on diorganodichlorosilanes and diorganotin dichlorides. Addition of the lithiated butadiene to trimethylchlorosilane and trimethyltin chloride yields products resulting from dehydrochlorination and multiple bond migration in the starting dichlorobutadiene.

Various 1,1-disubstituted stannoles based upon the 2,3,4,5-tetraphenylstannacyclopentadiene system have been synthesized and reported as part of this series of papers.<sup>1-2</sup> The parent stannole ring system is, however, unknown.

One possible approach is through the 1,4-dilithio derivative of the unsubstituted butadiene-1,3 by analogy with the now well-known and general reaction of the cis-,cis-1,4-dilithio-1,2,3,4-tetraphenylbutadiene with organometallic and metalloidal dihalides. The reaction of diorganotin dihalides, for example, affords a convenient route to the stannoles:<sup>3-6</sup>



The dihalo- precursor to the simple dilithio compound, 1,4-dichlorobuta-1,3-diene, can be prepared by the dimerization of 1,2-dichloroethylene with benzoyl peroxide and dechlorination of the resulting 1,3,4,4-tetrachlorobutene-1 by metallic zinc dust in methanol:<sup>7-10</sup>

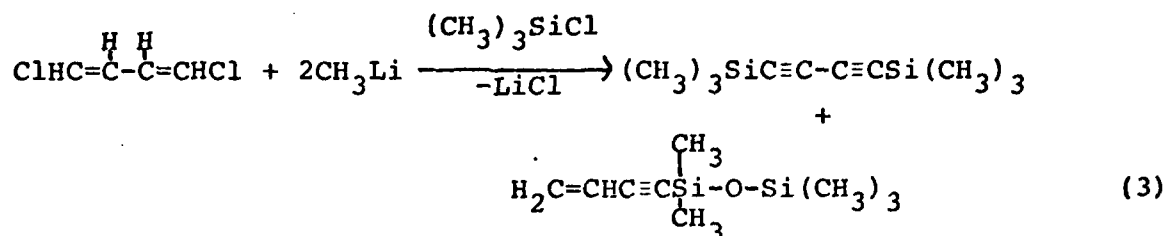


The infrared spectrum of the product showed the superimposition of bands arising from the cis-,cis-; cis-,trans- and trans-,trans- isomers of 1,4-dichlorobuta-1,3-diene.<sup>7</sup> The mass spectrum contained the parent ion as a polyisotopic peak at  $m/e = 126$ .

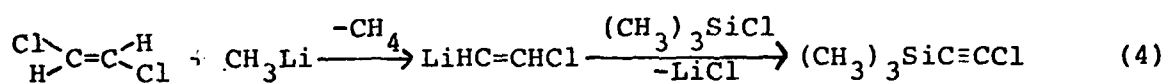
Unfortunately, treatment of the 1,4-dichlorobutadiene with conventional lithiating agents followed by addition of either diorganodichlorosilanes or diorganotin dichlorides results only in the polymerization of the starting material. The infusible white solid polymer leaves no silicon or tin(IV) oxide residue on burning, and exhibits in its infrared spectrum absorption bands at  $1638\text{ cm}^{-1}$  arising from a  $\text{-C=C-}$  stretching mode, a second at  $842\text{ cm}^{-1}$  which can be assigned to a  $\delta(\text{C-H})$  out-of-plane deformation mode and a broad band centered at  $650\text{ cm}^{-1}$  from a  $\nu(\text{C-Cl})$  mode. Carbonylation of the expected 1,4-dilithio intermediate did not give an unambiguous 1,4-dicarboxylic acid product on hydrolysis. Neither did reaction of trimethylchlorosilane or trimethyltin chloride give the expected 1,4-bis(trimethylmetalloidal) derivatives.

Addition of the 1,4-dichlorobutadiene lithiated by methyllithium to a solution of trimethylchlorosilane in ether gave a precipitate and a filtrate from which two silicon-containing products could be isolated, 1,4-bis(trimethylsilyl)buta-1,3-diyne, and what appears to be a trace of a hydrolysis or oxidation product from 1-trimethylsilylbuta-1-yne-3-ene which results during glc separation and collection:



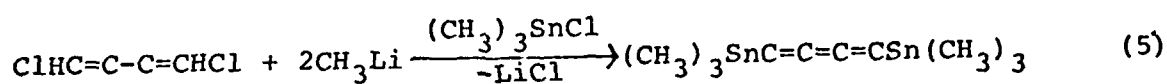


The 1,4-bis-(trimethylsilyl)buta-1,3-diyne is similar to the product of the treatment of 1,2-dichloroethylene with methyllithium followed by trimethylchlorosilane to give 1-trimethylsilyl-2-chloroacetylene:<sup>11</sup>



1,4-Bis(trimethylsilyl)butadiyne-1,3 has been synthesized by the dimerization of ethynyltrimethylsilane by the copper(I) chloride tetramethylethylenediamine complex in the presence of oxygen gas.<sup>12,13</sup>

Analogous reaction of the lithiated 1,4-dichlorobutadiene with trimethyltin chloride gave only one tin-containing product, 1,4-bis-(trimethyltin)butatriene, along with a large yield of the polymerized 1,4-dichlorobutadiene.



Thus both the silicon and tin reactions result in products which derive from dehydrochlorination and multiple bond migration in the starting 1,4-dichlorobutadiene.

## Experimental

### 1,3,4,4-Tetrachloro-1-butene

1,2-Dichloroethylene (430 g cis- and trans-mixture, b.p. 56-62°) was allowed to reflux for 14 days with dibenzoyl peroxide (4.5 g, mmols). After the removal of unreacted starting material, distillation gave the following fractions: b.p. 40-85.2° (18.5 mm), 10 g; b.p. 84.2-94.0° (18.5 mm), 160 g and b.p. 94.0-94.3° (18.5 mm), 1 g.

### Dechlorination

A solution of 1,3,4,4-tetrachloro-1-butene (140 g, second fraction, 0.73 mol) in methanol (140 mL) was added dropwise in the course of 105 min to a stirred suspension of zinc dust (315 g, 4.82 g-atoms) in methanol (420 mL). Toward the end of the addition the mixture was allowed to reflux gently. After stirring 24 hr at room temperature the hydrochloric acid solution was extracted with methylene chloride. Drying and evaporation of the organic solvent gave an oil which on distillation gave the following fractions: b.p. 29.5-37.0° (15-25 mm), 8.0 g; b.p. 31.5-35.0° (16.5 mm), 60.0 g and b.p. 35.0-60.0° (16.5 mm), 5.2 g. The total yield was 73.2 g (82% of theory).

The infrared spectrum showed bands at 3085(s), 3065(s), 1755(m,b), 1702(m,b), 1671(m,b), 1623(s), 1568(s), 1355(m), 1336(s), 1304(s,d), 1240(w), 1184(m,d), 1115(m), 1092(m), 950(s,sh), 910(m), 845(s), 805(s,sh), 765(s,b), 710(s), 598(m) and 495(m)  $\text{cm}^{-1}$ . The mass spectrum contained fragments up to  $m/e = 126$  which is the molecular ion. An abundant peak appeared at  $m/e = 122$ .

Reaction of Lithiated 1,4-Dichloro-1,3-butadiene with Trimethylchlorosilane

Methylolithium in ethyl ether (8.00 mL, 13.36 mmoles) was added dropwise to an ether solution of 1,4-dichloro-1,3-butadiene (2 g, 16.3 mmoles). The reaction was cooled in a Dry Ice/acetone bath under nitrogen and the temperature slowly raised to ambient. The brown-colored solution gave a brown-white colored suspension after stirring at room temperature for 2 hours. The lithium solution was added dropwise at  $-70^{\circ}$  to a solution of trimethylchlorosilane (4.1 mL, 31.99 mmoles) in ethyl ether (5 mL), and the temperature slowly raised to ambient. Refluxing 30 minutes gave a tan colored precipitate for which the infrared spectrum lacked the stretching frequency associated with the  $\text{Si}-(\text{CH}_3)_3$  group at  $750\text{ cm}^{-1}$ .

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5-42.5 (16.5 mm), 1.1 g (1,4-dichloro-1,3-butadiene); b.p. 75-78.0 (15 mm), 0.3 g  $\begin{array}{c} \text{H} \quad \text{H} \quad \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \quad | \quad | \\ \text{H}-\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\ \quad \quad \quad | \quad \quad | \\ \quad \quad \quad \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$  and b.p. 90-92.5 (10 mm), 0.9 g [1,4-bis(trimethylsilyl)-1,3-butadiyne].

The third fraction collected at 90-92.5° (10 mm) was found to be 1,4-trimethylsilyl-1,3-butadiyne (mp =  $107^{\circ}$ ; lit.<sup>12-13</sup> =  $107^{\circ}$ ). The infrared spectrum showed bands at 2960(s), 2900(m), 2065(s,sh), 1413(m), 1250(s), 850(s,b), 765(s), 708(m), 650(s), 557(s), 470(w) and  $382\text{ cm}^{-1}$ . The nmr spectrum in  $\text{CDCl}_3$  contained only a singlet at 0.76 ppm (lit.<sup>12</sup> = 9.85 ppm) for the trimethylsilyl protons.

The second fraction was separated and collected by gas chromatography [6 ft. column, 10% UC-W98 (silicone oil) 80-100 packing on Chromosorb W]. The infrared spectrum of the second fraction in

$\text{CDCl}_3$  contained two singlets at 9.82 and 9.86 in addition to the vinyl group proton multiplet. The proton integration ratio was found to be 1:4.4 = vinyl:methyl vs. the calculated ratio of 1:5. The mass spectrum of this fraction contained fragments up to  $m/e = 194$ . An abundant silicon-containing fragment appeared at  $m/e$  ( $^{28}\text{Si}$ ) = 143 and a less abundant fragment at  $m/e = 117$ . Anal. Calcd. for  $\text{C}_9\text{H}_{18}\text{Si}_2\text{O}$ : C, 54.58; H, 9.14. Found: C, 53.27; H, 7.12%.

Reaction of Lithiated 1,4-Dichloro-1,3-butadiene with Trimethyltin Chloride

Into a solution of trimethyltin chloride (6.26 g, 31.99 mmol) in ethyl ether (5 mL) the lithium reagent (13.36 mmol) prepared as above was added dropwise at  $-70^\circ$  and the temperature slowly raised to ambient. Refluxing for 30 minutes gave white-brown colored precipitate, for which the infrared spectrum lacked the stretching frequency of the  $\text{Sn}(\text{CH}_3)_3$  group at  $556\text{ cm}^{-1}$ .

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5–42.5 (16.5 mm), 1.2 g (1,4-dichloro-1,3-butadiene) and b.p. 55.0–58.8 (18.0 mm), 1.5 g (24.8% yield)  $[(\text{CH}_3)_3\text{Sn}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}=\text{C}=\text{CSn}(\text{CH}_3)_3]$ .

The infrared spectrum of the latter contained bands at 3060(w,sh), 2998(m), 2920(m), 2375(w), 1759(w), 1715(w), 1623(w), 1569(m), 1400(w,b), 1335(w), 1300(w,d), 1194(m), 1120(w), 1092(w), 950(m,sh), 840(m), 790(s,b), 550(s), 515(w) and  $325(\text{s,b})\text{ cm}^{-1}$ . The nmr spectrum in  $\text{CDCl}_3$  contained a singlet at 9.31 ppm with  $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})| = 56.1\text{ Hz}$ . In addition, the portion integration ratio was found to be 1:9 = vinyl:methyl vs. 1:9 calcd.

Acknowledgement

Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548. We thank M&T Chemicals, Inc. for the donation of organotin starting materials.

### References

- (1) For Part II of this series see: W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee and J. J. Zuckerman, submitted for publication.
- (2) W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee and J. J. Zuckerman, submitted for publication.
- (3) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas and S. Lehman, J. Am. Chem. Soc., 82(1960) 5099.
- (4) E. H. Braye, W. Hubel and I. Caplier, J. Am. Chem. Soc., 83(1961) 4406.
- (5) H. H. Freeman, J. Org. Chem. 27(1962) 2298.
- (6) J. G. Zavistoski and J. J. Zuckerman, J. Org. Chem., 34(1969) 4197.
- (7) P. D. Bartlett and G. E. H. Wallbillich, J. Am. Chem. Soc., 55(1969) 409.
- (8) H. G. Viele and E. Franchimont, Chem. Ber., 97(1964) 602.
- (9) R. Criegee, W. Horauf and W. D. Schellenberg, Chem. Ber., 86(1953) 126.
- (10) W. Bauer, Chimia, 5(1951) 147.
- (11) W. Steingross and W. Zeil, J. Organomet. Chem., 6(1966) 109.
- (12) D. M. Walton and F. Waugh, J. Organomet. Chem., 37(1972) 45.
- (13) I. A. Shikhiev, M. F. Shostakovskii and L. A. Kayutenko, Dokl. Akad. Nauk Azerb. SSR, 15(1959) 21.